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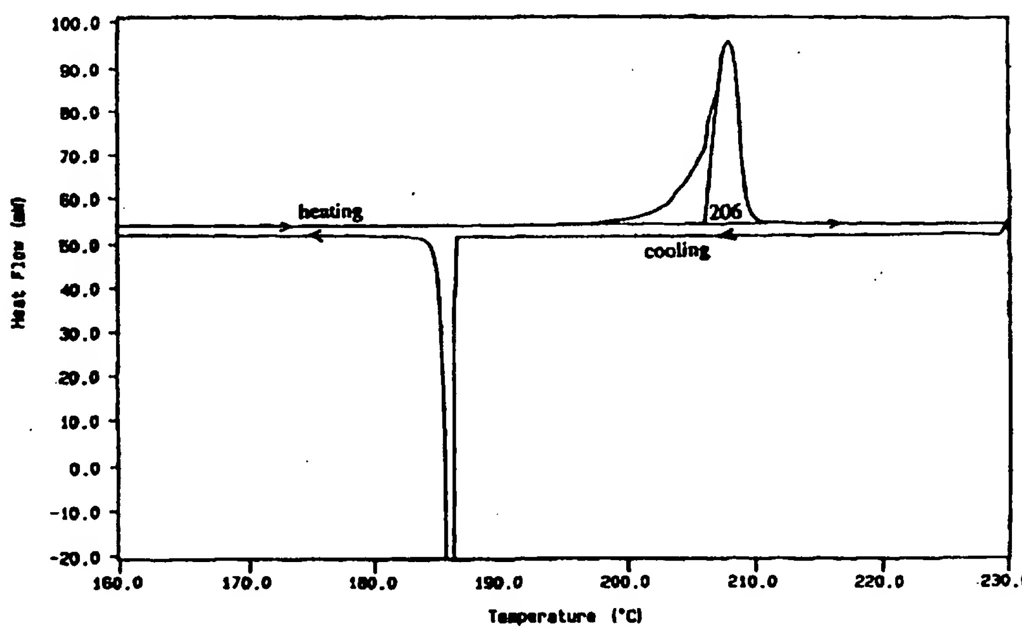

(57) Abstract

Lead-free solders are disclosed having relatively low melting temperatures, a small melting range, a small solidification range and a good flux response, making such alloys suitable for soldering and joining applications. The alloy compositions lie in the range of 86.2 % to 91.8 % tin, 3.2 % to 3.8 % silver, 5 % to 5.5 % indium, 0 % to 3 % bismuth, and 0 % to 1.5 % copper. The alloys have melting temperatures of less than 210 °C and melting ranges of less than 6 °C.

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TIN BASE SOLDER CONTAINS SILVER AND INDIUM

Background of the Invention

Presently, lead-tin alloys or variants of lead-tin alloys are used in many soldering and joining applications. The soldering technologies using these alloys are highly developed; however, these solders pose environmental and health hazards because they contain lead. Many states have passed legislation that will limit lead in container solders to 100ppm or less and the number of these states is increasing. The concern is leaching of lead into the water supply from landfills and into the atmosphere from incinerates. Electronics industries have been exempted at this time because no viable alternatives to lead-bearing solders are presently available. Even in the absence of any regulation, it is desirable that industries use lead-free solders to minimize lead exposure to employees and indirectly to the public at large.

Lead-bearing solders currently in use have many desirable properties, such as, low cost, availability, and engineering performance. However, lead is toxic to humans and wildlife when ingested or inhaled in large doses. Electronic circuits are typically disposed as solid waste in landfills. Waste products are generated during assembly of electronic boards. In lead-bearing solder manufacturing industries, solder dross can generate

lead-bearing dust, though the safety in such work areas is strictly controlled by the U.S. Occupational Safety and Health Administration (OSHA). Due to all these concerns, potential lead-free solders are to be designated to replace the lead-bearing alloys.

References of interest concerning the compositions and preparation of lead-free solders are U.S. patents 5,328,600 and 5,429,689.

Summary of the Invention

Traditional alloy developments involve preparation and testing of several alloys. Such alloy compositions generally have been chosen by trial and error or at best by empirical guidelines. As a result all relevant properties of the alloy have not been optimized simultaneously.

Applicants recognize that lead-free solders having different physical and mechanical properties are required for different applications. For example, lead-free solders that melt around 185° C and have a small solidification range are required for chip carrier-to-printed wiring board interconnections. The lead-free solders for automotive applications are required to have higher melting temperatures and better mechanical properties so that the joined components can withstand the thermomechanical fatigue caused by cyclic operation over

a wide temperature range. In all cases solderability should be good in order to make the lead-free solder a viable candidate for a particular application.

The term "lead-free" is here used to mean that lead is not deliberately added in the alloy; however, lead may be present in trace amounts in the elements considered in alloy design e.g., bismuth, copper, indium, silver and tin. The total lead content as impurity in the present alloys does not exceed the Federal specification QQ-S-571E at paragraph 3.2.1.1.1.

Applicants have established that the first and foremost criteria for compositions of lead-free solders of this invention are the melting temperature and the melting/solidification range. The compositions are based on extensive theoretical modelling of phase stability of tin-base binary and ternary phase diagrams. A database describing the phase stability and phase relations as a function of temperature and composition was created. The lead-free solders of this invention were established by imposing the following criteria: (i) melting temperature of the alloy should be less than 210° C, (ii) melting/solidification range should always be as small as possible (less than 6° C and preferably less than 5° C), (iii) composition sensitivity to melting point and melting/solidification range should be minimum, and (iv)

the amount of relatively expensive elements, such as Ag and In, should be minimum.

It is also desirable to have lead-free solders having hierarchical melting temperatures so that they can be used in different applications. The lead-free solders in this invention have good microstructural stability during solid-state aging, good physical properties, and can be manufactured into different shapes and forms, such as pigs, cakes, sheets, wires, powders, etc. The solders of the present invention provide joints with smooth and shiny appearance when Kester RMA flux is used in air.

The solder compositions of the present invention exclude lead, cadmium and zinc. The first two elements are toxic and hazardous to health and environment. Even though addition of zinc is helpful in lowering the melting point while keeping the melting range narrow, the wetting characteristics of zinc-containing solders are very poor due to the formation of dross unless highly activated flux is used. Furthermore, zinc-containing solders tend to oxidize excessively while making powders (for the solder paste). The essential ingredients of the compositions of the present invention are tin, silver, and indium, and optionally bismuth and copper, although other metals may be added to provide other properties.

In a preferred embodiment of the invention, the composition comprises from about 86.2% to 91.8% tin, 3.2% to 3.8% silver, 5% to 5.5% indium, 0% to 3% bismuth, and

0% to 1.5% copper. A particularly desirable composition is 87.6% tin, 3.4% silver, 5% indium, 3% bismuth and 1% copper.

Other features, advantages and objects of this invention will become apparent from the specification and drawing.

Drawing

Figure 1 is a differential scanning colorimeter (DSC) thermogram for a lead-free solder composed of 89.8% tin, 3.7% silver, 5% indium, and 1.5% copper.

Detailed Description of Preferred Embodiments

The alloy compositions of the present invention can be prepared by conventional techniques well known to the art. For example, weighed amounts of tin, silver, indium and bismuth can be placed in a crucible and the metals can be melted together using any conventional heating technique. When the metals have been heated to a temperature at which all the material is liquid, the material is homogonized and made into a powder or cast into suitable mold. After casting the alloy can be manufactured into various desired shapes and forms, such as rods, wires, cakes, sheets, foils etc.

A Perkin-Elmer differential scanning calorimeter (DSC-7) was used to determine melting and solidification behavior of the alloys. Stainless steel pans were used both in the reference and sample cells. Heating and cooling runs were performed at 5° C/min. In all alloys

described below, only one endothermic peak on melting and only one exothermic peak on solidification were observed. The melting temperature was determined by the intersection of tangent of the steepest slope and the baseline on heating. On cooling the alloys exhibit undercooling, the extent to which depends on many factors such as the alloy composition, substrate, cooling rate, etc. As an example, the DSC thermograms of 89.8% tin, 3.7% silver, 5% indium and 1.5% copper is shown in Figure 1.

The following examples present illustrative but non-limiting embodiments of the present invention. Unless otherwise indicated in the examples and elsewhere in the specification and claims, all parts and percentages are by weight.

Example 1

An alloy having composition 90.4% tin, 3.4% silver, 5.2% indium and 1% bismuth has melting temperature 209° C and a melting range of approximately 2° C.

Example 2

An alloy having composition 89.4% tin, 3.4% silver, 5.2% indium, 1% bismuth and 1% copper has melting temperature of 206° C and a melting range of approximately 5° C.

Example 3

An alloy having composition 89.8% tin, 3.7% silver, 5% indium and 1.5% copper has melting temperature 206° C and a melting range of approximately 2° C.

Example 4

An alloy having composition 88.8% tin, 3.7% silver, 5% indium, 1% bismuth and 1.5% copper has melting temperature 205° C and a melting range of approximately 3° C.

Example 5

An alloy having composition 88.6% tin, 3.4% silver, 5% indium, 2% bismuth and 1.0% copper has melting temperature 203° C and a melting range of approximately 4° C.

Example 6

An alloy having composition 87.6% tin, 3.4% silver, 5% indium, 3% bismuth and 1.0% copper has melting temperature 201° C and a melting range of approximately 6° C.

While the invention has been explained in relation to the preferred embodiments, it is to be understood that various modifications thereof will become apparent to those skilled in the art. The foregoing disclosure is not intended or to be construed to limit the present invention, or to otherwise exclude any such other embodiments, adaptations, variations and equivalent arrangements, the present invention being limited only by the claims appended hereto and the equivalents thereof.

The Claims

1. A lead-free solder alloy having 86.2% to 91.8% tin, 3.2% to 3.8% silver, 5% to 5.5% indium, 0% to 3% bismuth, and 0% to 1.5% copper.

2. The lead-free alloy of Claim 1, wherein the melting temperature is no more than 210° C.

3. The lead-free alloy of Claim 1, wherein the melting/solidification range is no more than 6° C.

4 The lead-free solder alloy of Claim 1 contains 90.4% tin, 3.4% silver, 5.2% indium and 1% bismuth.

5. The lead-free solder alloy of Claim 1 contains 89.4% tin, 3.4% silver, 5.2% indium, 1% bismuth and 1% copper.

6. The lead-free solder alloy of Claim 1 contains 89.8% tin, 3.7% silver, 5% indium and 1.5% copper.

7. The lead-free solder alloy of Claim 1 contains 88.8% tin, 3.7% silver, 5% indium, 1% bismuth and 1.5% copper.

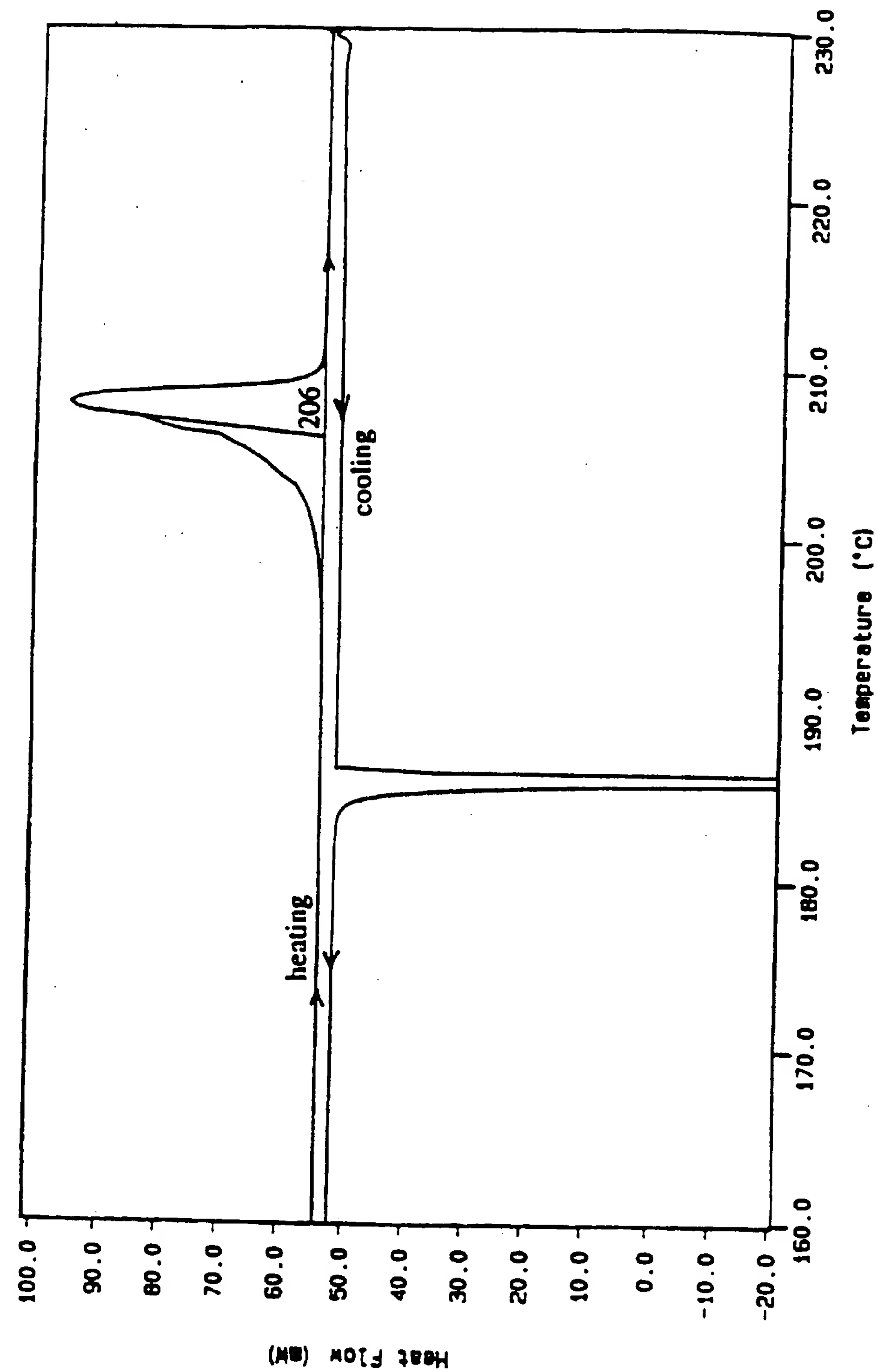
8. The lead-free solder alloy of Claim 1 contains 88.6% tin, 3.4% silver, 5% indium, 2% bismuth and 1.0% copper.

9. The lead-free solder alloy of Claim 1 contains 87.6% tin, 3.4% silver, 5% indium, 3% bismuth and 1.0% copper.

10. The lead-free solder alloy of Claim 1 taking a suitable form.

11. The lead-free solder alloy of Claim 10, said

suitable form comprising one or more of a powder, a rod, a wire, a cake, a sheet, or a foil.


206
cooling
heating
Temperature (°C)
Heat Flow (mW)
160.0
170.0
180.0
190.0
200.0
210.0
220.0
230.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
-10.0
-20.0

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US97/07376

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :C22C 13/02
US CL : 420/560, 561, 562; 148/400
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 420/560, 561, 562; 148/400

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

CAS ONLINE
search terms: tin or Sn, silver or Ag, indium or in, bismuth or bi,copper or cu

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X,P	US, 5,520,752 A (LUCEY, JR. et al.) 28 May 1996, claim 1.	1-11
X	EP 622151 A (CHEN et al.) 02 November 1994 (02.11.94), abstract.	1-11

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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